

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 05-285929

(43)Date of publication of application : 02.11.1993

(51)Int.Cl.

B28B 11/00

B28B 1/00

C04B 33/30

C04B 38/00

(21)Application number : 04-089112

(71)Applicant : TAKEDA CHEM IND LTD

(22)Date of filing : 09.04.1992

(72)Inventor : MORI MOTOYA
KIMURA TOSHIO

(54) METHOD FOR DRYING HOLLOW MOLDED ARTICLE

(57)Abstract:

PURPOSE: To prevent the cracking of a hollow molded article at the time of drying by molding the hollow molded article composed of an inorg. powder before forcibly passing air through the hollow part of the molded article.

CONSTITUTION: A hollow molded article is a molded article having a hollow part such as a tubular article, a honeycomb article or a foam article having open cells and one opened only at a single end thereof may be adapted but one opened at both ends thereof, especially, a honeycomb article is effective. After this molded article composed of an inorg. powder is molded, air is forcibly passed through the hollow part of the molded article. At this time, it is pref. to pass air only through the inner wall of the molded article. The drying of the molded article may be performed by this method until the dried molded article is obtained but this method is adapted until initial shrinkage due to drying is completed and, thereafter, a usual drying method such as high temp. standing drying or room temp. natural drying is used.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the
examiner's decision of rejection or application
converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of
rejection][Date of requesting appeal against examiner's decision
of rejection]

[Date of extinction of right]

* NOTICES *

JPO and INPIT are not responsible for any
damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The desiccation approach of the inorganic fine-particles moldings characterized by carrying out aeration to the centrum of this moldings compulsorily after shaping of the hollow-like moldings of inorganic fine particles.

[Claim 2] The desiccation approach according to claim 1 that a hollow-like moldings is a honeycomb-like moldings.

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.**** shows the word which can not be translated.

3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the new desiccation approach of the hollow-like moldings of inorganic fine particles.

[0002]

[Description of the Prior Art] Hollow-like moldingses, such as current and ceramics, are applied to various applications. For example, the ceramic honeycomb moldings is used for various applications, such as catalyst support and a filter. Moreover, the tubular ceramic moldings is used for the application of tubing for thermocouples, the protecting tube of a heating element, etc.

[0003] Water is added to a raw material, and it kneads or distributes, and fabricates and dries after an appropriate time, and the hollow-like moldings of inorganic fine particles, such as ceramics and activated carbon, is sintered if needed, and let it be a product.

[0004] When it dried under a room temperature or in the dryer in this desiccation process in the case of the hollow-like moldings, compared with the vapor rate of the moisture from the front face of the outer wall of a moldings, evaporation of the moisture from the front face of the wall of a moldings was slow, and had become the outer wall of a moldings, and the cause which produces the imbalance of a rate of drying inside and produces a crack.

[0005] Therefore, to dry evaporating moisture slowly at low temperature, or covering a moldings with vinyl etc. on the occasion of desiccation of the hollow-like moldings which the damage on a crack etc. tends to produce, and controlling evaporation of moisture was needed.

[0006] Moreover, in order to control the rapid desiccation in early stages of desiccation, there is also the approach of drying under high-humidity/temperature (the volume an exotic-material fabrication encyclopedia, 84-87 pages, and for "new-materials fabrication encyclopedia" edit committees, the Industrial Investigation Committees ingredient information-center issue).

[0007] However, even if it used this approach, little desiccation moldings of a crack was not able to be obtained. Moreover, the drying time will become very long.

[0008] Furthermore, blend thermal coagulation nature polysaccharide with inorganic fine particles, and heat a moldings, thermal coagulation nature polysaccharide is made to solidify, and the approach of subsequently drying this is also proposed (JP,3-131562,A). However, in this approach, in order that thermal coagulation nature polysaccharide may solidify, the process which presses down evaporation of moisture is needed.

[0009] By the above conventional approaches, the crack of a desiccation moldings cannot yet be prevented fully.

[0010] Moreover, in such a conventional method, if quite strict conditioning is not performed to a desiccation

process, a desiccation moldings is not producible. For this reason, even if workability and productive efficiency worsened or it carried out sufficient cautions depending on the desiccation moldings obtained, there was also a thing in which still more sufficient desiccation is impossible.

[0011] moreover, in spite of becoming disadvantageous on the property of a moldings, it is required to use many binders so that it may not crack -- etc. -- obliged to disadvantageous profit.

[0012]

[Problem(s) to be Solved by the Invention] Development of the desiccation approach of the hollow-like moldings of inorganic fine particles that the perfect desiccation moldings which does not have a crack etc. certainly is obtained by the simple approach was desired.

[0013]

[Means for Solving the Problem] After this invention person's having examined the hollow-like moldings of inorganic fine particles wholeheartedly and fabricating inorganic fine particles in the shape of hollow, when aeration of the air was compulsorily carried out to the opening of this moldings, even if it gave a subsequent elevated temperature and rapid desiccation, a desiccation moldings acquires the knowledge of being hard to produce the damage on a crack etc., repeats examination further, and came to complete this invention.

[0014] That is, this invention relates to the desiccation approach of the inorganic fine-particles moldings characterized by carrying out aeration to the centrum of this moldings compulsorily after shaping of the hollow-like moldings of inorganic fine particles.

[0015] The hollow-like moldings in this invention points out the thing of a moldings which has a centrum for the form which has a tubular moldings and honeycomb-like moldings and a free passage hole. Moreover, only one end face may be carrying out opening also of that in which the both ends of a moldings are carrying out opening. Especially this invention desiccation approach is suitable for that in which both ends are carrying out opening. It is especially effective in especially the honeycomb-like moldings of 20 - 95% of hole density. The configuration of this honeycomb hole may be the thing of arbitration, such as a polygon, a round shape, etc. of a trigonum, a rectangular head, etc.

[0016] Moreover, this centrum points out the opening section in tubing of a tubular moldings, the opening section of the cel hole of a honeycomb-like moldings, etc.

[0017] Moreover, although it is not especially restricted if the raw materials of a moldings are inorganic fine particles, industrial use ceramic fine particles, activated carbon, etc. are mainly applicable.

[0018] As industrial use ceramic fine particles, borides, such as nitrides, such as carbide, such as oxides, such as a silica, an alumina, a titania, a magnesia, a ferrite, synthetic cordierite, a zirconia, a zirconium dioxide, a mullite, a spinel, barium titanate, and a zeolite, silicon carbide, and boron carbide, silicon nitride, boron nitride, and aluminium nitride, zirconium boride, and titanium boride, a kaolin, talc, sepiolite, hydroxyapatite, etc. can be mentioned.

[0019] Especially this invention drying method is effective in desiccation of the moldings of a thing with quick desiccation like a zeolite.

[0020] Such a zeolite especially may not be limited but may be any of natural zeolite and permutite. Moreover, two or more sorts may be mixed and used. As such natural zeolite, a CHABA site mold, a natural mordenite mold, a clinoptilolite mold, an erionite mold, etc. are mentioned. As permutite, anything of the mold of A molds (the siluton BTM by Mizusawa Industrial Chemicals, Ltd., MIZUKA sieves 4ATM, etc.), X types (MIZUKA sieves XTM by Mizusawa Industrial Chemicals, Ltd. etc.), Y molds (MIZUKA sieves YTM by Mizusawa Industrial Chemicals, Ltd. etc.), a synthetic mordenite mold, and high silica molds (MFI mold etc.) is used. Furthermore, the thing from which a Si/aluminum atomic ratio and structure differ, the zeolite which consists of other elements can be used.

[0021] Moreover, it is usually easy to be used as a binder added in case the compound for shaping of inorganic fine particles is adjusted.

[0022] For example, mineral matter, such as natural polysaccharide, such as synthetic resins, such as polyvinyl alcohol, a polyvinyl butyral, polyethylene RENGUNIKORU, and a cellulosic, an alginic acid, gum arabic, a dextrin, curdlan, and a paramylum, clay, and a kaolin, etc. is used.

[0023] 1-50 weight section use of these binders is usually carried out to inorganic fine particles.

[0024] For example, also by the usual desiccation approach, although there are comparatively few cracks, in 1 - 30% of the weight of a case, it becomes easy to produce a crack at a desiccation process, when a zeolite is fabricated in the shape of a honeycomb, and there are more binder additions than 30 % of the weight.

[0025] Usually, a binder and the water of optimum dose are added to the aforementioned inorganic fine particles, the compound of inorganic fine particles is prepared, and then this is fabricated in the shape of a honeycomb, or the configuration of a request of tubular **.

[0026] Although not limited, especially the shaping approach can apply extrusion molding, injection molding, etc.

as the shaping approach, when using water for compound preparation.

[0027] Thus, a desiccation moldings without a crack is obtained by giving the obtained moldings to this invention desiccation approach. What is necessary is just to specifically ventilate compulsorily to the centrum of this hollow-like moldings after shaping of an inorganic fine-particles moldings. Since the desiccation inside a moldings (wall) is promoted by this process, the difference of the rate of drying of a moldings outside surface and the interior decreases, the strain of the moldings generated in early stages of desiccation is suppressed, and the reinforcement of a moldings is also maintained by it. This early desiccation influences the reinforcement of a moldings greatly, and the damage on a crack etc. cannot produce easily the moldings obtained by doing in this way in a subsequent desiccation process.

[0028] Especially this approach of ventilating compulsorily is not limited. The method of specifically placing a hollow-like moldings into the dryer which the powerful fan took the side of at the approach and dryer which place a hollow-like moldings so that the sense of a wind and the sense of a hole may become the same, and the diffuser of the wind of a compressor etc. can be done. Moreover, the approach of attracting the air which exists in a centrum with a vacuum pump etc. is also applicable.

[0029] In this case, it is desirable to make only the internal cel part (wall) of a hollow-like moldings ventilate by the approach of carrying out a lap with the approach of extracting the outlet of air and controlling ventilation, the nonwoven fabric which made only the outer wall part of a hollow-like moldings become wet with a synthetic-resin film or water. According to this approach, the desiccation moldings which does not have a crack in the whole hollow-like moldings rather than the approach of ventilating and drying for a short time is obtained.

[0030] The air which carries out aeration may be atmospheric air, usual warm air, or usual hot blast. The air under the usual workplace conditions, for example, a room temperature and the condition of the usual humidity, can be used. 150 degrees C or less of temperature are 5-120 degrees C preferably more highly than 0 degree C, and, specifically, 80% or less of relative humidity (R. H.) is good. Furthermore, it is preferably [70% or less of] good.

[0031] There should just be airflow as air passes the hole of a moldings, and it is suitably decided with a configuration, magnitude, etc. of the moldings to dry. For example, although the both ends of a moldings are carrying out opening, to a case, air should just pass from one opening edge to the opening edge of another side. Moreover, what is necessary is just to circulate the air of the centrum of a moldings by the approach of attracting the air which exists in the approach of spraying a compressed air from the direction of an opening edge, or the centrum etc., when opening only of one end face is being carried out.

[0032] Although desiccation of a moldings may be completely dried until it obtains a desiccation moldings by this invention desiccation approach, until it is not necessary to dry completely on the other hand and the initial contraction of the moldings by desiccation is completed. Generally, it is sufficient if it dries to constant-rate-period termination extent the first stage. What is necessary is just to define aeration time amount suitably according to the raw material used, since this initial contraction changes with classes of inorganic fine particles.

[0033] What is necessary is just to use the usual desiccation approaches, such as standing desiccation in an elevated temperature, and an air drying in a room temperature, after that initial desiccation, in order to obtain a perfect desiccation moldings in ending aeration with this initial desiccation extent. For example, if it puts in into a 115-degree C dryer immediately, a moldings can be dried in 1 - 2 hours after initial desiccation.

[0034] Furthermore, after drying a moldings, it can sinter and a desired inorganic fine-particles sintering object can be obtained as occasion demands.

[0035]

[Effect of the Invention] According to this invention, in case a hollow-like moldings is dried, the crack of the moldings at the time of desiccation can prevent simple by making a moldings wall ventilate air.

[0036] The honeycomb-like moldings by which the desiccation process was conventionally presupposed especially that it is difficult and takes time and effort by this approach is able to manufacture simple efficiently.

[0037]

[Example]

50g (solid content) bentonite powder (Ben Clay TM by Mizusawa Industrial Chemicals, Ltd.), a 50g glass fiber (the Nippon Sheet Glass Co., Ltd. make, micro glass chopped strand TMRES015), and 200g (solid content) kibushi clay (Maruo Calcium make) were added to the high silica type composition zeolite powder (MIZUKA sieves EX[by Mizusawa Industrial Chemicals, Ltd.]-122TM) of 700g of manufactures of the [example -1 of manufacture] zeolite honeycomb moldings (solid content). Furthermore, 12.5g curdlan (Takeda Chemical Industries, Ltd. make), the 31.3g hydroxypropyl methylcellulose (viscosity in 20 degrees C of a 2 % of the weight water solution: about 28,000 centipoises), and a 6.2g polyethylene glycol (the Sanyo Chemical Industries, Ltd. make, macrogol 6000 TM) were added, and this mixture was blended dryly with the desk 2 shaft kneading machine for about 1 hour.

[0038] Subsequently, it kneaded under reduced pressure (about 100 to 700 mmHg) for about 1 hour so that a water total amount might become this mixture with 440g about distilled water. In this kneading, the jacket of a kneading machine was made to circulate through 10-degree C cold water, and the kneading object was cooled.

[0039] Thus, the obtained kneading object was put into the polyethylene bag, and it riped at a room temperature thru/or 40 degrees C for about three - five days. Next, the extruding press machine (DE[by Honda Machinery Works Co., Ltd.]-35 mold) was loaded with this, it kneaded under reduced pressure, and the kneading solid-state constituent for zeolite shaping was obtained.

[0040] Next, the above-mentioned extruding press machine was equipped with the honeycomb molding die, the above-mentioned kneading constituent was built using this, and extrusion molding was carried out to the shape of a prism mold honeycomb of 30mmx30mm wide, and the number 300-piece [/square] inch of cels.

[0041] Next, this was cut in die length of 40mm, and the honeycomb-like moldings was obtained.

[0042] To the cel hole of the zeolite honeycomb moldings obtained in the example -1 of [example -1] manufacture, the 24-degree C compressed air was ventilated for 30 seconds 2.5k g/cm2 and R.H.:0%. This compressed air extracted the nozzle, and it is made to touch only the wall of a cel hole, and it touched the honeycomb outer wall, and it went so that there might be nothing.

[0043] Then, this honeycomb moldings was given to the air drying of 24 hours under 24 degrees C and an R.H.:43% condition, and the desiccation moldings was obtained.

[0044] Five desiccation moldingses were created like the above. The crack property is shown in [Table 1].

[0045] To the cel hole of the zeolite honeycomb moldings obtained in the example -1 of [example -2] manufacture, the 24-degree C compressed air was ventilated for 30 seconds 2.5k g/cm2 and R.H.:0%. The ventilation by this compressed air extracted the nozzle, and it is made to touch only the wall of a cel hole, and it touched the honeycomb outer wall, and it went so that there might be nothing.

[0046] Then, this honeycomb moldings was given to stoving of 2 hours under 115 degrees C and an R.H.:1% condition, and the desiccation moldings was obtained.

[0047] Five desiccation moldingses were created like the above. The crack property is shown in [Table 1].

[0048] To the cel hole of the zeolite honeycomb moldings obtained in the example -1 of [example -3] manufacture, 80-degree C warm air was ventilated for 120 seconds R.H.:3%. Ventilation by this warm air was performed by [as touching a cel hole and a honeycomb outer wall].

[0049] Then, this honeycomb moldings was given to stoving of 2 hours under 115 degrees C and an R.H.:1% condition, and the desiccation moldings was obtained.

[0050] Five desiccation moldingses were created like the above. The crack property is shown in [Table 1].

[0051] To the cel hole of the zeolite honeycomb moldings obtained in the example -1 of [example -4] manufacture, 80-degree C warm air was ventilated for 30 seconds R.H.:3%. Under the present circumstances, it is made not to plug up the opening edge of a honeycomb moldings, and the lap only of that outer wall was carried out with the synthetic-resin film, and as warm air mainly touched the wall of a cel hole, it carried out.

[0052] Then, this honeycomb moldings was given to stoving of 2 hours under 115 degrees C and an R.H.:1% condition, with the lap carried out, and the desiccation moldings was obtained.

[0053] Five desiccation moldingses were created like the above. The crack property is shown in [Table 1].

[0054] To the cel hole of the zeolite honeycomb moldings obtained in the example -1 of [example -5] manufacture, 80-degree C warm air was ventilated for 30 seconds R.H.:3%. The ventilation by this warm air extracted the nozzle, and it is made to touch only the wall of a cel hole, and it touched the honeycomb outer wall, and it went so that there might be nothing.

[0055] Then, this honeycomb moldings was given to stoving of 2 hours under 115 degrees C and an R.H.:1% condition, and the desiccation moldings was obtained.

[0056] Five desiccation moldingses were created like the above. The crack property is shown in [Table 1].

[0057] When 700 degrees C and baking of 2 hours were performed within the electric furnace (Product made from MOTOYAMA, SUPER BURN SB-2025D mold), the crack with new all etc. did not generate the desiccation moldings obtained in the [example -6] examples 1-5, but the good baking object was obtained.

[0058] The honeycomb moldings obtained in the example -1 of the [example -1 of comparison] manufacture was given to the air drying of 24 hours under 24 degrees C and an R.H.:43% condition, and the desiccation moldings was obtained.

[0059] Five desiccation moldingses were created like the above. The crack property is shown in [Table 1].

[0060] The honeycomb moldings obtained in the example -1 of the [example -2 of comparison] manufacture was given to stoving of 2 hours under 115 degrees C and an R.H.:1% condition, and the desiccation moldings was obtained.

[0061] Five desiccation moldingses were created like the above. The crack property is shown in [Table 1].

[0062] It is made not to plug up the opening edge of the honeycomb moldings obtained in the example -1 of the

[example -3 of comparison] manufacture, the lap of the outer wall was carried out with the synthetic-resin film, stoving of 2 hours was given under 115 degrees C and an R.H.:1% condition, and the desiccation moldings was obtained.

[0063] Five desiccation moldingses were created like the above. The crack property is shown in [Table 1].

[0064]

[Table 1]

表 1.

| | ゼオライト ハニカム | 1 | 2 | 3 | 4 | 5 |
|------|---|---|---|---|---|---|
| 1. | ①圧空 (24℃ R. H. = 0% 2.5kg/cm ²) 30秒 セルの中のみ通風 ②自然乾燥 | ◎ | ◎ | ◎ | ◎ | ◎ |
| 2 | ①圧空 (24℃ R. H. = 0% 2.5kg/cm ²) 30秒 セルの中のみ通風 ②加熱乾燥 (115℃ R. H. = 1% 2時間) | ○ | ○ | ○ | ○ | ○ |
| 3. | ①温風乾燥 (80℃ R. H. = 3%) 120秒 ハニカム全体通風 ②加熱乾燥 (115℃ R. H. = 1% 2時間) | ◎ | ◎ | ○ | ○ | ○ |
| 4. | ①温風乾燥 (80℃ R. H. = 3%, ラッパに託) 30秒 ハニカム全体通風 ②加熱乾燥 (115℃ R. H. = 1% 2時間, ラッパに託) | ◎ | ◎ | ◎ | ◎ | ◎ |
| 5. | ①温風乾燥 (80℃ R. H. = 3%) 30秒 セルの中のみ通風 ②加熱乾燥 (115℃ R. H. = 1% 2時間) | ◎ | ◎ | ◎ | ◎ | ◎ |
| 比 1. | 自然乾燥 (24℃ R. H. = 43% 24時間) | ○ | ○ | × | × | × |
| 比 2. | 加熱乾燥 (115℃ R. H. = 1% 2時間) | × | × | × | × | × |
| 比 3. | 加熱乾燥 (115℃ R. H. = 1%, ラッパに託) | ○ | ○ | ○ | × | × |

× 不良 (ハニカム内部に多数ひび割れあり)

○ 良好 (1～2ヶ所 わずかにクラックが発生)

◎ 優秀 (全くひび割れなし)

[0065] The 125g binder for ceramic shaping (the Takeda Chemical Industries, Ltd. make, BIOPORI TMP-1) was added to the alumina (the Showa Denko K.K. make, AL-160SG-4) of 2,500g of manufactures of the [example -2 of manufacture] alumina honeycomb moldings (solid content), and this mixture was blended dryly with the desk 2 shaft kneading machine for about 1 hour.

[0066] Subsequently, it kneaded under reduced pressure (about 100 to 700 mmHg) for about 1 hour so that it might become this mixture with 500g about distilled water. In this kneading, the jacket of a kneading machine was made to circulate through 10-degree C cold water, and the kneading object was cooled.

[0067] Thus, the obtained kneading object was put into the polyethylene bag, and it riped at a room temperature thru/or 40 degrees C for about three - five days. Next, the extruding press machine (DE[by the Honda ironworker company]-35 mold) was loaded with this, it kneaded under reduced pressure, and the kneading solid-state constituent for alumina shaping was obtained.

[0068] Next, the above-mentioned extruding press machine was equipped with the honeycomb molding die, and extrusion molding of the above-mentioned kneading constituent was carried out to the shape of a prism mold honeycomb of 30mm by 30mm, and the number 300-piece [/square] inch of cels using this.

[0069] This was cut in die length of 40mm inheriting, and the honeycomb-like moldings was obtained.

[0070] To the cel hole of the alumina honeycomb moldings obtained in the example -2 of [example -7] manufacture, 80-degree C warm air was ventilated for 30 seconds R.H.:3%.

[0071] Then, this honeycomb moldings was given to stoving of 2 hours under 115 degrees C and an R.H.:1% condition, and the desiccation moldings was obtained.

[0072] Five desiccation moldingses were created like the above. The crack property is shown in [Table 2].

[0073] When 1,600 degrees C and baking of 2 hours were performed within the electric furnace (Product made from MOTOYAMA, the SUPER BURN SB-2025D mold TM), the crack with new all etc. did not generate the desiccation moldings obtained in the [example -8] example -7, but the good baking object was obtained.

[0074] The honeycomb moldings obtained in the example -2 of the [example -4 of comparison] manufacture was given to stoving of 2 hours under 115 degrees C and an R.H.:1% condition, and the desiccation moldings was

obtained.

[0075] Five desiccation moldings were created like the above. The crack property is shown in [Table 2].

[0076]

[Table 2]

表 2.

| | アルミナ ハニカム | 1 | 2 | 3 | 4 | 5 |
|------|--|---|---|---|---|---|
| 7. | ①温風乾燥 (80℃ R. H. = 3%) 30分 ハニカム全体通風 ②加熱乾燥 (115℃ R. H. = 1% 2時間) | ◎ | ◎ | ◎ | ◎ | ◎ |
| 比 4. | 加熱乾燥 (115℃ R. H. = 1% 2時間) | ○ | ○ | × | × | × |

× 不良 (ハニカム内部に多数ひび割れあり)

○ 良好 (1～2ヶ所 わずかにクラックが発生)

◎ 優秀 (全くひび割れなし)

[Translation done.]

| | | | | |
|--------------------------|----------------------|-----------|---------|-------------------------|
| (51)Int.Cl. ^s | 識別記号 | 庁内整理番号 | F I | 技術表示箇所 |
| B 2 8 B 11/00 | | Z 9152－4G | | |
| 1/00 | | E 9152－4G | | |
| | | F 9152－4G | | |
| C 0 4 B 33/30 | | | | |
| 38/00 | 3 0 3 | Z | | |
| 審査請求 未請求 請求項の数 2 (全 6 頁) | | | | |
| (21)出願番号 | 特願平4－89112 | | (71)出願人 | 000002934 |
| | | | | 武田薬品工業株式会社 |
| (22)出願日 | 平成 4 年(1992) 4 月 9 日 | | | 大阪府大阪市中央区道修町四丁目 1 番 1 号 |
| | | | (72)発明者 | 毛利 元哉 |
| | | | | 茨城県土浦市乙戸南 3 丁目 5 番 4 号 |
| | | | (72)発明者 | 木村 俊雄 |
| | | | | 茨城県石岡市大字石岡2205番地の 7 |
| | | | (74)代理人 | 弁理士 岩田 弘 (外 4 名) |

(54)【発明の名称】 中空状成形物の乾燥方法

(57)【要約】

【目的】無機粉体の中空状成形物の新規な乾燥方法を提供する。

【構成】無機粉体の中空状成形物の成形後、該成形物の中空部に強制的に通気することを特徴とする無機粉体成形物の乾燥方法。

【効果】簡便であり、確実にひび割れ等のない完全な乾燥成形物が得られた。

【特許請求の範囲】

【請求項1】無機粉体の中空状成形物の成形後、該成形物の中空部に強制的に通気することを特徴とする無機粉体成形物の乾燥方法。

【請求項2】中空状成形物がハニカム状成形物である請求項1記載の乾燥方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、無機粉体の中空状成形物の新規な乾燥方法に関する。

【0002】

【従来の技術】現在、セラミックス等の中空状成形物は、種々の用途に応用されている。例えば、セラミックスハニカム成形物は触媒担体やフィルターなど様々な用途に利用されている。また、管状セラミックス成形物は熱電対用の管や発熱体の保護管などの用途に利用されている。

【0003】セラミックスや活性炭などのような無機粉体の中空状成形物は、原料に水を加えて練合または分散し、しかる後成形および乾燥し、必要に応じて焼結して製品とされている。

【0004】中空状成形物の場合、この乾燥工程において、室温下あるいは、乾燥機中で乾燥を行なうと、成形物の外壁の表面からの水分の蒸発速度に比べて、成形物の内壁の表面からの水分の蒸発が遅く、成形物の外壁と、内部で乾燥速度のアンバランスを生じ、ひび割れを生じる原因となっていた。

【0005】従って、ひび割れなどの損傷が生じ易い中空状成形物の乾燥に際しては、低温で緩慢に水分を蒸発させるとか、成形物をビニール等で覆うなどして水分の蒸発をコントロールしながら乾燥を行うことが必要とされていた。

【0006】また、乾燥初期の急激な乾燥を抑制するため、高温高湿下で乾燥する方法もある（新材料成形加工事典、84～87頁、「新素材成形加工事典」編集委員会編、(株)産業調査会材料情報センター発行）。

【0007】しかし、この方法を用いても、ひび割れの少ない乾燥成形物を得ることはできなかった。また、乾燥時間が非常に長くなってしまふ。

【0008】更には、熱凝固性多糖類を無機粉体に配合し、成形物を加熱して熱凝固性多糖類を凝固させ、次いでこれを乾燥する方法も提案されている（特開平3-131562）。しかし、この方法においては、熱凝固性多糖類が凝固するために、水分の蒸発を押さえる工程が必要となる。

【0009】前述のような従来方法では、未だ十分に乾燥成形物のひび割れを防止することができていない。

【0010】また、このような従来法では、乾燥工程にかなり厳密な条件設定を施さなければ、乾燥成形物が生産できない。このため、作業性、生産効率が悪くなった

り、得られる乾燥成形物によっては十分な注意をしてもなお、十分な乾燥が不可能なものもあった。

【0011】また、成形物の特性上不利となるにも拘らず、ひび割れしないように多くのバインダーを使用することが必要であるなど不利益を余儀なくされていた。

【0012】

【発明が解決しようとする課題】簡便な方法により、確実にひび割れ等のない完全な乾燥成形物が得られるような無機粉体の中空状成形物の乾燥方法の開発が望まれていた。

【0013】

【課題を解決するための手段】本発明者は、無機粉体の中空状成形物について鋭意検討を行ない、無機粉体を中空状に成形した後に、該成形物の空隙へ強制的に空気を通気したところ、その後の高温での急速な乾燥に付しても乾燥成形物は、ひび割れなどの損傷が生じにくいという知見を得、更に検討を重ね、本発明を完成するに至った。

【0014】すなわち、本発明は無機粉体の中空状成形物の成形後、該成形物の中空部に強制的に通気することを特徴とする無機粉体成形物の乾燥方法に関する。

【0015】本発明における中空状成形物とは、管状成形物、ハニカム状成形物、連通孔を有するフォームなど、中空部を有する成形物のことを指す。また、成形物の両端が開口しているものでも、一方の端面だけが開口しているものでもよい。特に本発明乾燥方法は、両端が開口しているものに適している。とりわけ、開孔率20～95%のハニカム状成形物に特に有効である。該ハニカム孔の形状は、三角、四角等の多角形や円形など、任意のものであって良い。

【0016】また、該中空部とは、管状成形物の管内の空隙部やハニカム状成形物のセル孔の空隙部などを指す。

【0017】また、成形物の原料は無機粉体であれば、特に制限されるものではないが、主として工業用セラミックス粉体や活性炭などが対象となる。

【0018】工業用セラミックス粉体としては、シリカ、アルミナ、チタニア、マグネシア、フェライト、合成コージェライト、ジルコニア、酸化ジルコニウム、ムライト、スピネル、チタン酸バリウム、ゼオライトなどの酸化物、炭化ケイ素、炭化ホウ素等の炭化物、窒化ケイ素、窒化ホウ素、窒化アルミニウム等の窒化物、ホウ化ジルコニウム、ホウ化チタン等のホウ化物、カオリン、タルク、セピオライト、ヒドロキシアパタイトなどを挙げることができる。

【0019】ゼオライトのように乾燥の速いものの成形物の乾燥に、本発明乾燥法は特に有効である。

【0020】このようなゼオライトは、特に限定されず、天然ゼオライトおよび合成ゼオライトのいずれであってもよい。また、二種以上を混合して使用しても良

い。このような天然ゼオライトとしては、チャバサイト型、天然モルデナイト型、クリノプチロライト型、エリオナイト型等が挙げられる。合成ゼオライトとしてはA型（水澤化学工業(株)製シルトンBTM、ミズカシーブス4ATM等）、X型（水澤化学工業(株)製ミズカシーブスXTM等）、Y型（水澤化学工業(株)製ミズカシーブスYTM等）、合成モルデナイト型、ハイシリカ型（MF1型等）のいずれの型のものも用いられる。更には、Si/A1原子比や構造の異なるもの、また、他元素から構成されるゼオライト等も用いることができる。

【0021】また、無機粉体の成形用コンバウンドを調整する際に添加するバインダーとしては、通常、使われるもので良い。

【0022】例えば、ポリビニルアルコール、ポリビニルブチラール、ポリエチレングリコール、セルロース誘導体などの合成樹脂類、アルギン酸、アラビアゴム、デキストリン、カードラン、バラミロンなどの天然多糖類、粘土、カオリンなどの無機物質などが使用される。

【0023】これらバインダーは通常、無機粉体に対して、1～50重量部使用される。

【0024】例えば、ゼオライトをハニカム状に成形した際には、バインダー添加量が30重量%より多い場合には通常の乾燥方法でも比較的ひび割れが少ないが、1～30重量%の場合には乾燥工程でひび割れが生じ易くなる。

【0025】通常、前記の無機粉体にバインダーと適量の水を加え、無機粉体のコンバウンドを調製し、次にこれをハニカム状や管状等の所望の形状に成形する。

【0026】成形方法は、特に限定されるものではないが、コンバウンド調製に水を使用する場合には、成形方法として、押出し成形、射出成形などを適用することができる。

【0027】このようにして得られた成形物を本発明乾燥方法に付すことによって、割れのない乾燥成形物が得られる。具体的には、無機粉体成形物の成形後、該中空状成形物の中空部へ強制的に通風すればよい。この工程により、成形物内部（内壁）の乾燥が促進されるため、成形物外表面と内部との乾燥速度の差が少なくなり、乾燥初期に発生する成形物のひずみが抑えられ成形物の強度も保たれる。この初期の乾燥が成形物の強度に大きく影響し、このようにして得られた成形物はその後の乾燥工程においても、ひび割れなどの損傷が生じにくい。

【0028】この強制的に通風する方法は特に限定されない。具体的には、強力なファンの付いた乾燥機中に、中空状成形物を風の向きと孔の向きが同じになるように置く方法、ドライヤーや、コンプレッサーの風の吹き出し口に、中空状成形物を置く方法などができる。また、真空ポンプ等により中空部に存在する空気を吸引する方法も適用できる。

【0029】この際に、空気の出口を絞り通風を制御す

る方法や、中空状成形物の外壁部分のみを合成樹脂フィルムや水で湿らせた不織布等でラップする方法によって、中空状成形物の内部セル部分（内壁）のみに、通風させることが好ましい。この方法によると、中空状成形物全体に通風・乾燥する方法よりも、短時間で、ひび割れのない乾燥成形物が得られる。

【0030】通気させる空気は通常の大気や温風または熱風であってもよい。通常の作業場条件下、例えば、室温、通常の湿度の条件下の空気をを用いることができる。

10 具体的には、温度は0℃より高く150℃以下、好ましくは5～120℃で、相対湿度（R.H.）は80%以下が良い。更に好ましくは70%以下がよい。

【0031】風量は成形物の孔を空気が通過するだけあれば良く、乾燥する成形物の形状や大きさ等によって適宜決められる。例えば、成形物の両端が開口しているもの場合には、一方の開口端から他方の開口端へ空気が通過すればよい。また、一方の端面のみ開口している場合には、開口端の方から圧空を吹き付ける方法や中空部に存在している空気を吸引する方法などにより、成形物
20 の中空部の空気を流通させればよい。

【0032】成形物の乾燥は、本発明乾燥方法によって乾燥成形物を得るまで完全に乾燥してもよいが、一方、完全に乾燥してしまう必要はなく、乾燥による成形物の初期収縮が終了するまでもよい。一般に、恒率乾燥期終了程度まで初期乾燥すれば足りる。この初期収縮は無機粉体の種類によって異なるので、使用される原料に応じて、適宜、通気時間は定めればよい。

【0033】この初期乾燥程度で通気を終了する場合には、その初期乾燥後、完全な乾燥成形物を得るために、
30 高温での静置乾燥、室温での自然乾燥など通常の乾燥方法を用いれば良い。例えば、初期乾燥後、直ちに115℃の乾燥機中に入れると、1～2時間で成形物の乾燥を行うことができる。

【0034】更に成形物を乾燥後、必要により、焼結し、所望の無機粉体焼結物を得ることができる。

【0035】

【発明の効果】本発明によれば、中空状成形物を乾燥させる際に、空気を成形物内壁に通風させることにより乾燥時の成形物のひび割れが簡便に防止できる。

40 【0036】この方法により、従来、特に、乾燥工程が困難で手間がかかるとされていたハニカム状成形物が効率良く簡便に製造することが可能である。

【0037】

【実施例】

〔製造例-1〕ゼオライトハニカム成形物の製造

700グラム（固形分）のハイシリカ型合成ゼオライト粉末（水澤化学工業（株）製ミズカシーブスEX-122TM）に、50グラム（固形分）のベントナイト粉末（水澤化学工業（株）製ベンクレイTM）、50グラムの
50 ガラス繊維（日本板硝子（株）製、マイクログラスチョ

ップドストランドTM RES015) 及び200グラム (固形分) の木節粘土 (丸尾カルシウム製) を加えた。更に、12.5グラムのカードラン (武田薬品工業 (株) 製) 及び31.3グラムのヒドロキシプロピルメチルセルロース (2重量%水溶液の20℃における粘度: 約28,000センチポイズ) および6.2グラムのポリエチレングリコール (三洋化成工業 (株) 製, マクロゴール6000TM) を加え、この混合物を卓上二軸混練機で約1時間、乾式混合した。

【0038】次いで、この混合物に蒸留水を水総量が440グラムとなるように加えて、減圧下 (約100~700mmHg) に約1時間、混練した。この混練において、混練機のジャケットには10℃の冷水を循環させ、混練物を冷却した。

【0039】このようにして得られた混練物をポリエチレン袋に入れ、約3~5日間、室温乃至40℃で熟成した。次に、これを押出成形機 (本田鐵工社製 DE-35型) に装填し、減圧下に混練して、ゼオライト成形用混練固体組成物を得た。

【0040】次に、ハニカム成形用金型を、上記押出成形機に装着し、これを用いて、上記混練組成物をたて30mm×よこ30mm、セル数300個/平方インチの角柱型ハニカム状に押出成形した。

【0041】次にこれを長さ40mmに切断し、ハニカム状成形物を得た。

【0042】[実施例-1] 製造例-1で得られたゼオライトハニカム成形物のセル孔に、2.5kグラム/cm²、R.H.: 0%、24℃の圧空を30秒間通風した。この圧空はノズルを絞り、セル孔の内壁のみに接するようにし、ハニカム外壁には接し無いように行った。

【0043】その後、該ハニカム成形物を、24℃、R.H.: 43%の条件下に24時間の自然乾燥に付して、乾燥成形物を得た。

【0044】上記と同様にして、5個の乾燥成形物を作成した。その割れ特性を〔表1〕に示す。

【0045】[実施例-2] 製造例-1で得られたゼオライトハニカム成形物のセル孔に、2.5kグラム/cm²、R.H.: 0%、24℃の圧空を30秒間通風した。この圧空による通風はノズルを絞り、セル孔の内壁のみに接するようにし、ハニカム外壁には接し無いように行った。

【0046】その後、該ハニカム成形物を、115℃、R.H.: 1%の条件下に2時間の加熱乾燥に付して、乾燥成形物を得た。

【0047】上記と同様にして、5個の乾燥成形物を作成した。その割れ特性を〔表1〕に示す。

【0048】[実施例-3] 製造例-1で得られたゼオライトハニカム成形物のセル孔に、R.H.: 3%、80℃の温風を120秒間通風した。この温風による通風はセル孔およびハニカム外壁に接するようにして行った。

【0049】その後、該ハニカム成形物を、115℃、R.H.: 1%の条件下に2時間の加熱乾燥に付して、乾燥成形物を得た。

【0050】上記と同様にして、5個の乾燥成形物を作成した。その割れ特性を〔表1〕に示す。

【0051】[実施例-4] 製造例-1で得られたゼオライトハニカム成形物のセル孔に、R.H.: 3%、80℃の温風を30秒間通風した。この際、ハニカム成形物の開口端をふさがないようにし、その外壁のみを合成樹脂フィルムでラップし、温風が主にセル孔の内壁に接するようにして行った。

【0052】その後、該ハニカム成形物を、ラップしたまま、115℃、R.H.: 1%の条件下に2時間の加熱乾燥に付して、乾燥成形物を得た。

【0053】上記と同様にして、5個の乾燥成形物を作成した。その割れ特性を〔表1〕に示す。

【0054】[実施例-5] 製造例-1で得られたゼオライトハニカム成形物のセル孔に、R.H.: 3%、80℃の温風を30秒間通風した。この温風による通風は、ノズルを絞り、セル孔の内壁のみに接するようにし、ハニカム外壁には接し無いように行った。

【0055】その後、該ハニカム成形物を、115℃、R.H.: 1%の条件下に2時間の加熱乾燥に付して、乾燥成形物を得た。

【0056】上記と同様にして、5個の乾燥成形物を作成した。その割れ特性を〔表1〕に示す。

【0057】[実施例-6] 実施例1~5で得られた乾燥成形物を電気炉 ((株)モトヤマ製、SUPER BURN SB-2025D型) 内で、700℃、2時間の焼成を行ったところ、いずれも新たなひび割れ等は発生せず、良好な焼成物が得られた。

【0058】[比較例-1] 製造例-1で得られたハニカム成形物を、24℃、R.H.: 43%の条件下に24時間の自然乾燥に付して、乾燥成形物を得た。

【0059】上記と同様にして、5個の乾燥成形物を作成した。その割れ特性を〔表1〕に示す。

【0060】[比較例-2] 製造例-1で得られたハニカム成形物を、115℃、R.H.: 1%の条件下に2時間の加熱乾燥に付して、乾燥成形物を得た。

【0061】上記と同様にして、5個の乾燥成形物を作成した。その割れ特性を〔表1〕に示す。

【0062】[比較例-3] 製造例-1で得られたハニカム成形物の開口端をふさがないようにし、その外壁を合成樹脂フィルムでラップし、115℃、R.H.: 1%の条件下に2時間の加熱乾燥に付して、乾燥成形物を得た。

【0063】上記と同様にして、5個の乾燥成形物を作成した。その割れ特性を〔表1〕に示す。

【0064】

〔表1〕

表1.

| | ゼオライト ハニカム | 1 | 2 | 3 | 4 | 5 |
|-----|---|---|---|---|---|---|
| 1. | ①圧空 (24℃ R.H. = 0% 2.5kg/cm ²) 30秒 セルの中心部通風 ②自然乾燥 | ◎ | ◎ | ◎ | ◎ | ◎ |
| 2. | ①圧空 (24℃ R.H. = 0% 2.5kg/cm ²) 30秒 セルの中心部通風 ②加熱乾燥 (115℃ R.H. = 1% 2時間) | ○ | ○ | ○ | ○ | ○ |
| 3. | ①温風乾燥 (80℃ R.H. = 3%) 120秒 ハニカム全体通風 ②加熱乾燥 (115℃ R.H. = 1% 2時間) | ◎ | ◎ | ○ | ○ | ○ |
| 4. | ①温風乾燥 (80℃ R.H. = 3% ラッパ状) 30秒 ハニカム全体通風 ②加熱乾燥 (115℃ R.H. = 1% 2時間 ラッパ状) | ◎ | ◎ | ◎ | ◎ | ◎ |
| 5. | ①温風乾燥 (80℃ R.H. = 3%) 30秒 セルの中心部通風 ②加熱乾燥 (115℃ R.H. = 1% 2時間) | ◎ | ◎ | ◎ | ◎ | ◎ |
| 比1. | 自然乾燥 (24℃ R.H. = 43% 24時間) | ○ | ○ | × | × | × |
| 比2. | 加熱乾燥 (115℃ R.H. = 1% 2時間) | × | × | × | × | × |
| 比3. | 加熱乾燥 (115℃ R.H. = 1% ラッパ状) | ○ | ○ | ○ | × | × |

× 不良 (ハニカム内部に多数ひび割れあり)

○ 良好 (1~2ヶ所 わずかにクラックが発生)

◎ 優秀 (全くひび割れなし)

【0065】【製造例-2】アルミナハニカム成形物の製造

2,500グラム (固形分) のアルミナ (昭和電気(株)製、AL-160SG-4) に125グラムのセラミックス成形用バインダー (武田薬品工業(株)製、ヒオポリマーTM P-1) を加え、この混合物を卓上二軸混練機で約1時間、乾式混合した。

【0066】次いで、この混合物に蒸留水を500グラムとなるように加えて、減圧下 (約100~700mmHg) に約1時間、混練した。この混練において、混練機のジャケットには10℃の冷水を循環させ、混練物を冷却した。

【0067】このようにして得られた混練物をポリエチレン袋に入れ、約3~5日間、室温ないし40℃で熟成した。次に、これを押出成形機 (本田鉄工社製DE-35型) に装填し、減圧下に混練して、アルミナ成形用混練固体組成物を得た。

【0068】次に、ハニカム成形用金型を、上記押出成形機に装着し、これを用いて、上記混練組成物を、たて30mm×よこ30mm、セル数300個/平方インチの角柱型ハニカム状に押出成形した。

【0069】繼ぐに、これを長さ40mmに切断し、ハ

ニカム状成形物を得た。

【0070】【実施例-7】製造例-2で得られたアルミナハニカム成形物のセル孔に、R.H.: 3%、80℃の温風を30秒間通風した。

【0071】その後、該ハニカム成形物を、115℃、R.H.: 1%の条件下に2時間の加熱乾燥に付して、乾燥成形物を得た。

【0072】上記と同様にして、5個の乾燥成形物を作成した。その割れ特性を〔表2〕に示す。

【0073】【実施例-8】実施例-7で得られた乾燥成形物を電気炉 ((株)モトヤマ製、SUPER BURN SB-2025D型TM) 内で、1,600℃、2時間の焼成を行ったところ、いずれも新たなひび割れ等は発生せず、良好な焼成物を得られた。

【0074】【比較例-4】製造例-2で得られたハニカム成形物を、115℃、R.H.: 1%の条件下に2時間の加熱乾燥に付して、乾燥成形物を得た。

【0075】上記と同様にして、5個の乾燥成形物を作成した。その割れ特性を〔表2〕に示す。

【0076】

〔表2〕

表2.

| | アルミナ ハニカム | 1 | 2 | 3 | 4 | 5 |
|-----|--|---|---|---|---|---|
| 7. | ①温風乾燥(80℃ R. H. = 3%) 30分 ハニカム全体通風 ②加熱乾燥(115℃ R. H. = 1% 2時間) | ◎ | ◎ | ◎ | ◎ | ◎ |
| 比4. | 加熱乾燥(115℃ R. H. = 1% 2時間) | ○ | ○ | × | × | × |

× 不良(ハニカム内部に多数ひび割れあり)

○ 良好(1~2ヶ所 わずかにクラックが発生)

◎ 優秀(全くひび割れなし)